Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for "Relativistic Nonorthogonal Configuration Interaction: Application to $L_{2,3}$-Edge X-ray Spectroscopy"

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1 Oscillator Strength Test

We used a simple model system to test the implementation of NOCI, which allowed us to compare to another code base (in this case Gaussian). We used ethylene with a complete active space of 2 electrons in 2 orbitals without optimizing the orbitals. In this case, the CASCI (Gaussian) and NOCI (ChronusQ) results should be the same. Furthermore, to test the nonorthogonal part of the code we introduced nonzero overlaps between the ground state and one of the determinants for the S_1 state. This was accomplished by mixing the π and π^* orbitals together using a simple rotation matrix. Then during the NOCI calculation, the redundant component is removed, and should ideally yield the same results as the orthogonal determinant expansion. Thus, we were able to test the relevant observables across several orders of magnitude with respect to the overlap. The results are presented in Figure 1. Overall, we observed exactly the same results for both the frequencies and oscillator strengths across the range of overlaps. Furthermore, the oscillator strength for the S_1 state agrees with

Gaussian to at least six significant figures.

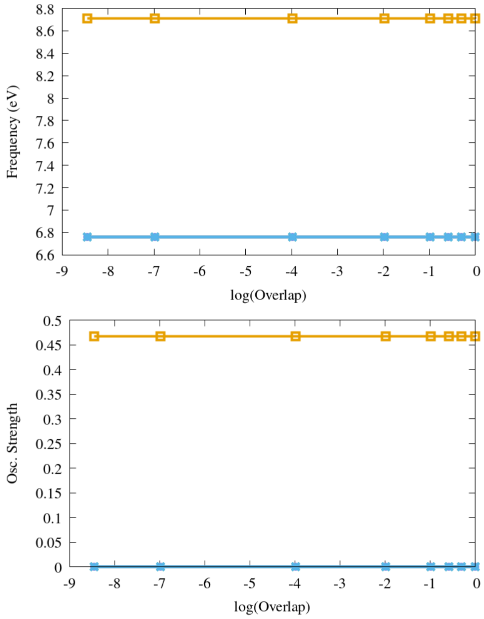

Figure 1: The frequencies and oscillator strengths of ethylene using Generalized-Hartree-Fock(unoptimized) orbitals in a complete active space (2 electrons, 2 orbitals) with respect to the overlap. An overlap was introduced by mixing the π and π^* orbitals for one of the determinants in S_1 state. Here, orange is the S_1 state and blue are the triplet states.

2 Determinant Optimization

To investigate the effect of spin-orbit coupling, we optimized the determinants with and without spin-orbit coupling to see the effect that it has on the spectra. These calculations were performed using the same geometry, but a smaller basis set was used (def2-svp).[1] Additionally, only a subset of the determinants were used. Here were excited the 2p electrons into the first eight virtual orbitals, which is enough to capture the low energy peaks of the L-edge spectrum. We have provided the spectra in Figure 2.

First, when spin-orbit coupling is not included at all, the L_2 and L_3 edges are not split into $p_{1/2}$ and $p_{3/2}$ peaks, which demonstrates the necessity of including spin-orbit coupling. However, adding spin-orbit coupling perturbatively splits the peaks. Overall, the variational and perturbative approximations yield similar spectra for this system. Here, the L_3

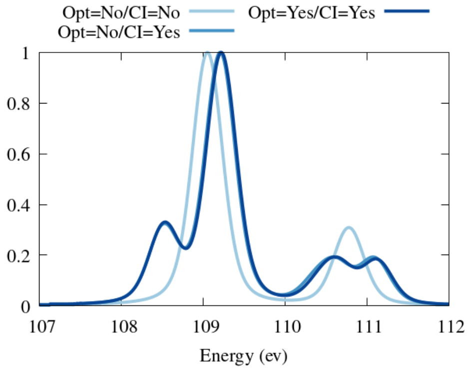

Figure 2: L-edge X-ray absorption spectra for $SiCl_4$ using various approximations: 1). Total neglect of spin-orbit coupling (Opt=No/CI=NO), 2). Perturbative approach that only includes spin-orbit coupling in the NOCI, but not in the orbital optimization (Opt=No/CI=Yes), 3). Fully variational spin-orbit coupling (Opt=Yes,CI=No).

edge is almost identical for both determinant expansions. However, the L_2 edge features a very modest blue-shift when the determinants are variationally optimized with spin-orbit coupling.

3 $SiCl_4$

Table 1: Spin-orbit splitting of the first set of peaks (104-105 eV) in the $SiCl_4$ $L_{2,3}$-edge spectra, and the number of basis functions used in each system and timing to compute the NOCI.

Method	$\Delta E(eV)$	N_B	$t_{NOCI}^{Unscaled}(s)$	t_{NOCI}^{Scaled}
Sapporo-DZP	0.59	90	6342.3	6250.0
Sapporo-DZP-diffuse	0.60	135	11346.5	11086.0
Sapporo-TZP	0.63	170	25261.3	23820.5
Sapporo-TZP-diffuse	0.63	250	69795.1	676610.0
Experiment	0.61	-	-	-

References

(1) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys.*

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